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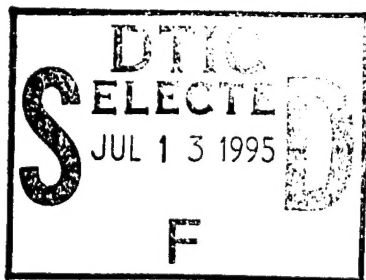
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Tetramethylammonium Phenyltrialkylborates in the Photoinduced Electron Transfer Reaction with Benzophenone. Generation of Alkyl Radicals and Their Addition to Activated Alkenes.

Polykarpov, A.; ; Neckers, D. C. *Tetrahedron Letters*, 1995 in press.



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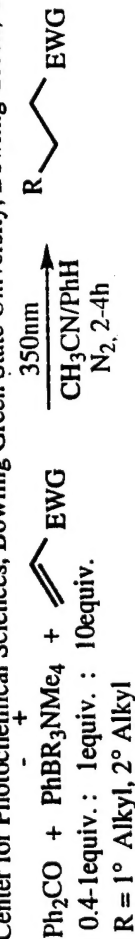
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Tetramethylammonium Phenyltrialkylborates in the Photoinduced Electron Transfer Reaction with Benzophenone. Generation of Alkyl Radicals and Their Addition to Activated Alkenes.

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Photoinduced one electron oxidation of tetramethylammonium phenyltrialkylborates by benzophenone triplet leads to formation of substantially more than one equivalent of alkyl radicals. The adducts of alkyl radicals to various electron poor alkenes are produced in good yields. No phenyl radical adducts are observed.

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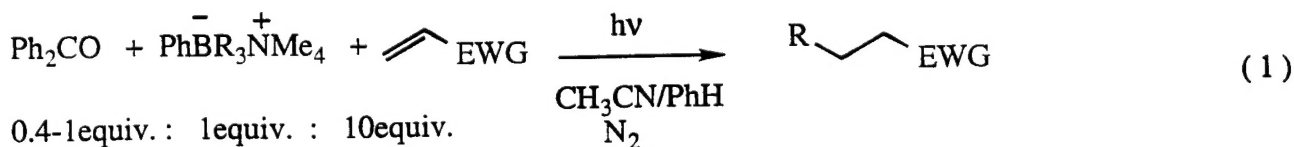
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Abstract: Photoinduced one electron oxidation of tetramethylammonium phenyltrialkylborates by the excited state of benzophenone in an acetonitrile/benzene solution containing an excess of activated alkene produces substantially more than one equivalent of the alkyl radicals. The corresponding adducts of alkyl radicals to the alkenes are produced in good yields. No phenyl radical adducts are observed.

Trialkylboranes are known to produce alkyl group addition products to certain olefins under various conditions.² Though radical mechanisms are suggested, in the majority only one alkyl group of three may be used in subsequent reaction processes. Unlike α,β -unsaturated ketones and aldehydes, α,β -unsaturated esters and nitriles do not readily undergo addition reactions with organoboranes by most of the reported processes³. Though it has been reported that ethyl esters of acrylic and methacrylic acids react with organoboranes to form conjugate addition products under electrolytic conditions, less than one equivalent of alkyl group was transferred from the boranes.⁴

Photochemical oxidation of triarylalkylborates has been subject of intensive activity in the open and patent literature since cyanine borates were first discovered to initiate acrylate photopolymerization.⁵ Trialkylaryl borates, on the other hand, have been much less extensively studied. In this communication we describe preliminary studies of the addition of primary and secondary alkyl radicals generated by single electron transfer from tetramethylammonium phenyltrialkylborates to benzophenone triplet to various activated alkenes (eq. 1). In contrast to the other systems,² substantially more than one equivalent of alkyl radicals may be generated using our reaction, and the reaction is general. Efficient radical additions are reported for a variety of electron poor olefins.



The addition of phenyl anion to trialkylboranes, available from alkenes (method A) or reaction of dichlorophenylboron with three equivalents of the alkyl anion (method B) followed by cation exchange (in water for most borates except those containing C₆ and longer hydrocarbon chains) gives various tetramethylammonium phenyltrialkylborates in good yields (eq. 2). Most borate salts are water insoluble

solids, relatively stable to air and moisture. Acetonitrile solutions of these borates show no absorbance above 300nm. Yields of tetramethylammonium phenyltrialkylborates obtained by these methods and ^{11}B nmr data are given in Table 1. The X-ray diffraction structure shows tetramethylammonium phenyltriethylborate to be tetrahedral (Figure 1).

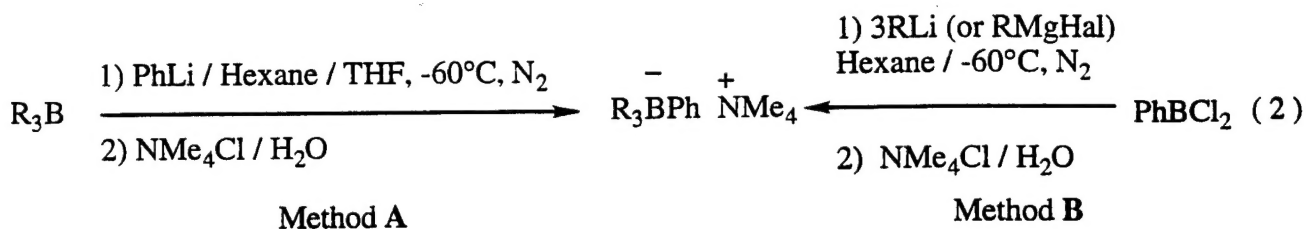
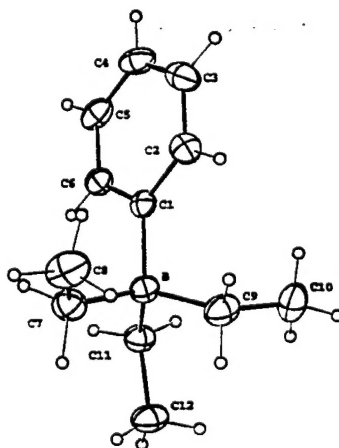


Table 1. Yields^a and ^{11}B NMR Data for Tetramethylammonium Phenyltrialkylborates ($\text{PhBR}_3\text{NMe}_4$).

Entry	R	Yield (%)	δ (ppm)	Entry	R	Yield (%)	δ (ppm)
1	Methyl ^b	70	-33.89 ^c	6	Cyclopentyl	90	-32.44
2	Ethyl	95	-33.07	7	Cyclohexyl	75	-31.60
3	sec-Butyl	82	-30.16	8	Cycloheptyl	76	-29.36
4	n-Hexyl	68	-33.96	9	Norbornyl	95	-31.35
5	n-Octyl	61	-34.04	10	n-Bu ₄ BNMe ₄ ^d	92	-36.86

^aOverall yields. ^bObtained through method B from methyllithium (other borates were made via procedure A). ^cIn d₆-DMSO, $\delta(\text{B}(\text{OMe})_3)=0$ ppm. ^dTetramethylammonium tetra-n-butylborate, readily available from tri-n-butylborane and n-butyllithium, is given for comparison. It possesses good reactivity in the radical addition. As with other tetraalkylborates, it is less stable than the phenyltrialkylborates.

Figure 1. Molecular Structure of Tetramethylammonium Phenyltriethylborate (only the anion is shown).



Irradiation (Rayonet, 350nm, water cooling, 25°C, 2-4 hours) of a solution (under nitrogen) containing borate (5mM), benzophenone (2-5mM) and an activated alkene (50mM) in benzene/acetonitrile (5:1 v/v) gives adducts in good yields. Yields of the adducts of ethyl radicals generated from tetramethylammonium phenyltriethylborate to a variety of activated alkenes are presented in Table 2.

Table 2. Yields of Adducts^a of Ethyl Radicals Generated From Tetramethylammonium Phenyltriethylborate to Various Activated Alkenes.

Entry	Alkene	Adduct	Yield (%)
1	n-Butyl acrylate ^b	n-Butyl pentanoate	190 ^c
2	Methyl methacrylate ^b	Methyl 2-methylpentanoate	184
3	Phenyl vinylsulfone	Phenyl n-butylsulfone	(168) ^d
4	Diethyl maleate	Diethyl ethylsuccinate	(160)
5	Diethyl vinylphosphonate	Diethyl n-butylphosphonate	(153)
6	Acrylonitrile ^b	Valeronitrile	(145)
7	N,N-Dimethyl acrylamide	N,N-Dimethyl valeroamide	119
8	Styrene	n-Butylbenzene	73

^aAll the products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures. Yields are based on borate used. ^bUsed with inhibitor. ^cDetermined by GC. ^dIsolated Yields.

The results of the addition of alkyl radicals generated from tetramethylammonium phenyltrialkylborates to n-butyl methacrylate are given in Table 3. Though the mechanism of the reaction is not completely understood, and lithium phenyltrialkylborates have been found to be significantly less reactive (sometimes completely unreactive) than the corresponding tetramethylammonium salts under the conditions discussed above, the initial step is anticipated to be an electron transfer from borate to benzophenone triplet state followed by formation of the alkyl radical and phenyldialkylborane.⁵ Alkyl radicals form because they are of greater stability and phenyl radical products (biphenyl, phenyl adducts) were not detected by GC (less than 0.1%). Such alkyl radicals, when formed, add to the alkene. Phenyldialkylborane is also capable of initiating a chain radical reaction. It can react either with the oxygen centered radical product of addition of the alkyl radical to the alkene or with the triplet state of benzophenone^{3,6} forming additional radicals. Benzophenone is usually recovered (10-40%). Water soluble and polar boron containing products have yet to be studied.

The preliminary results outlined in this communication indicate that photoinitiated oxidation of tetramethylammonium phenyltrialkylborates, easily accessible from alkenes via hydroboration followed by the addition of phenyl anion and further cation exchange, leads to formation of substantially more

than one equivalent of the adducts. Further studies are under way to define the mechanism more clearly and to extend these investigations to other systems involving different excited state acceptors, alkenes and various borates:

Table 3. Yields of Adducts^a in the Addition of Primary and Secondary Alkyl Radicals Generated From Various Tetramethylammonium Phenyltrialkylborates to n-Butyl Methacrylate^b.

Entry	R	Adduct	Yield (%)
1	Methyl	n-Butyl 2-methylbutanoate	90
2	Ethyl	n-Butyl 2-methylpentanoate	193
3	sec-Butyl	n-Butyl 2,4-dimethylhexanoate	236
4	n-Octyl	n-Butyl 2-methylundecanoate	(221) ^c
5	n-Hexyl	n-Butyl 2-methylnonanoate	(169)
6	Cyclopentyl	n-Butyl 3-cyclopentyl-2-methylpropanoate	(240)
7	Cyclohexyl	n-Butyl 3-cyclohexyl-2-methylpropanoate	(175)
8	Cycloheptyl	n-Butyl 3-cycloheptyl-2-methylpropanoate	(185)
9	Norbornyl	n-Butyl 3-norbornyl-2-methylpropanoate	(227)

^aYields are based on borate consumed and determined by GC. ^bUsed with inhibitor. ^cYields were determined after isolation by flash chromatography (silica gel, hexanes / ethyl acetate 40/1).

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